Supplemental information for

?-donor Olefin Substituents Alter Olefin Binding to $CpFe(CO)_2^+$

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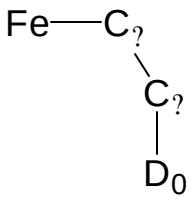
Table 1. Selected Distances (Å) and Angles (deg) for $CpFe(CO)_2[H_2CCHNMe_2]^+$

			X-ray	DFT
Fe(1)	C(2)		2.0903(9)	2.109
Fe(1)	C(3)		2.0980(10)	2.113
Fe(1)	C(4)		2.1100(10)	2.126
Fe(1)	C(5)		2.1230(10)	2.147
Fe(1)	C(6)		2.0988(10)	2.125
Fe(1)	C(7)		1.7675(10)	1.766
Fe(1)	C(9)		1.7689(9)	1.760
Fe(1)	C(11)		2.1143(10)	2.113
Fe(1)	C(12)		2.823(11)	2.799
C(2)	C(3)		1.4041(14)	1.415
C(2)	C(6)		1.4334(14)	1.434
C(3)	C(4)		1.4243(14)	1.420
C(4)	C(5)		1.4139(15)	1.417
C(5)	C(6)		1.4143(15)	1.436
C(7)	O(8)		1.1449(12)	1.145
C(9)	O(10)		1.1425(11)	1.149
C(11)	C(12)		1.4290(13)	1.423
C(12)	N(13)		1.3015(11)	1.315
N(13)	C(14)		1.4604(12)	1.462
N(13)	C(15)		1.4641(12)	1.463
C(7)	Fe(1)	C(9)	95.66(4)	94.6
C(7)	Fe(1)	C(11)	87.13(4)	86.0
C(9)	Fe(1)	C(11)	94.72(4)	94.6
O(8)	C(7)	Fe(1)	176.41(9)	179.1
O(10)	C(9)	Fe(1)	175.48(8)	178.3
C(12)	C(11)	Fe(1)	103.97(6)	102.9
N(13)	C(12)	C(11)	127.31(8)	128.2
C(12)	N(13)	C(14)	123.28(8)	123.3
C(12)	N(13)	C(15)	120.80(8)	121.3
C(14)	N(13)	C(15)	115.92(7)	115.3
C(11)	Fe(1)	C(7)	87.13(4)	86.0
C(11)	Fe(1)	C(9)	94.72(4)	94.6

Table 2. Selected Distances (Å) and Angles (deg) for $CpFe(CO)_2[CH_2CH(OEt)]^+$

		X-ray		DFT
Fe(1)	C(2)	2.073(10)		N/A
Fe(1)	C(3)	2.077(7)		N/A
Fe(1)	C(4)	2.103(6)		N/A
Fe(1)	C(5)	1.792(6)		1.774
Fe(1)	C(7)	1.849(10)		1.775
Fe(1)	C(9)	2.109(10)		2.156
Fe(1)	C10)	2.402(10)		2.585
C(2)	C(3)	1.383(9)		N/A
C(3)	C(4)	1.395(8)		N/A
C(4)	C(4)#1	1.401(10)		N/A
C(5)	O(6)	1.132(7)		1.143
C(7)	O(8)	1.133(13)		1.144
C(9)	C(10)	1.336(14)		1.391
C(10)	O(11)	1.359(12)		1.303
O(11)	C(12)	1.448(10)		1.460
C(12)	C(13)	1.425(12)		1.509
C(5)	Fe(1)	C(7)	89.2(5)	93.8
C(5)	Fe(1)	C(9)	83.8(5)	82.9
C(7)	Fe(1)	C(9)	100.1(3)	97.2
C(5)	Fe(1)	C(10)	113.7(4)	111.4
C(7)	Fe(1)	C(10)	85.3(5) 80.1	80.1
C(3)	C(2)	C(3)#1	109.2(9)	N/A
C(2)	C(3)	C(4)	107.5(7)	N/A
C(3)	C(4)	C(4)#1	107.8(4)	N/A
O(6)	C(5)	Fe(1)	178.7(6)	178.6
O(8)	C(7)	Fe(1)	174.8(11)	177.7
C(10)	C(9)	Fe(1)	85.3(8)	91.0
C(9)	C(10)	O(11)	121.0(9)	121.7
C(9)	C(10)	Fe(1)	61.1(6)	56.5
C(13)	C(12)	O(11)	114.2(10)	108.3

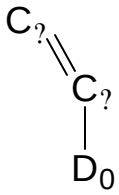


Occupancies of bonding orbitals and lone pair orbitals

D_0=	**F**	**N**	**O**
D_0-$C_ß$	1.99585	1.98910 + 1.95720	1.99350
$C_ß$-C_a	1.99387 + 1.62307	1.98457	1.98626
LP $C_ß$	N/A	N/A	0.78438
LP D_0	1.98804	N/A	1.96092
	1.96547		1.71971
	1.89044		

Natural charge (Q)

D_0=	**F**	**N**	**O**
Q Fe	-0.16299	-0.15648	-0.14524
Q C_a	-0.57008	-0.68182	-0.64036
Q $C_ß$	0.26798	0.15463	0.27859
Q D_0	-0.29729	-0.33933	-0.46819



Occupancies of bonding orbitals and lone pair orbitals on the free olefin

D_0=	**F**	**N**	**O**
D_0-$C_ß$	1.99640	1.98505	1.97748
$C_ß$-C_a	1.99657 + 1.99874	1.98899 + 1.98544	1.99365 + 1.99412
LP $C_ß$	N/A	N/A	N/A
LP D_0	1.99194	1.75413	1.96565
	1.96968		1.82567
	1.91042		

Natural charge (Q) on the free olefin

D_0=	**F**	**N**	**O**
Q C_a	-0.57079	-0.58519	-0.61063
Q $C_ß$	0.22706	-0.02879	0.12963
Q D_0	-0.33938	-0.46023	-0.53373